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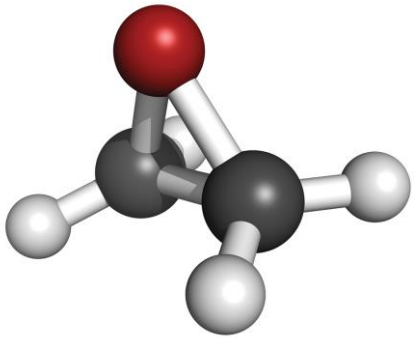
THE QUEEN'S AWARDS FOR ENTERPRISE: INNOVATION 2019

Ethylene oxide: techniques for sample collection and overcoming the challenges of the analysis.



Hannah Calder
Markes International
hcalder@markes.com

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- Background
- Challenges associated with monitoring ethylene oxide
  - Stability
  - Interferents
  - Sensitivity
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- Analytical performance (preliminary)
- Applying this to US EPA draft method 327
- Areas of interest for further investigation

Why the focus on Ethylene oxide?

Background

- Toxicity level re-assessed (2016)
- EtO 100-in-1-million cancer risk level: **11ppt**
- Measured at NATTS since 2019

Method 327 03/30/2023

METHOD 327 - Fugitive and Area Source Measurement of Selected Volatile Organic Hazardous Air Pollutants Using Specially Prepared Canisters

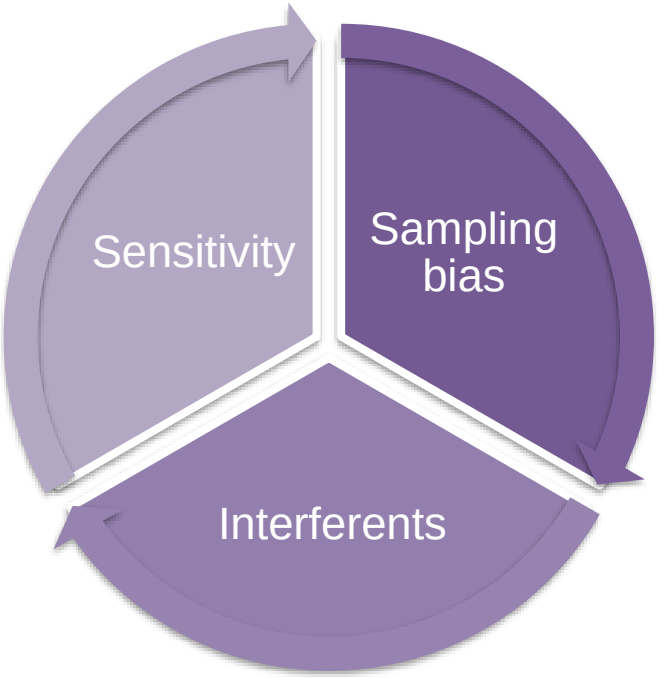
1.0 *Scope and Application*

1.1 This method describes the sampling and analysis of emissions from fugitive and area sources collected using specially prepared canisters and analyzed using a gas chromatograph (GC) coupled with a low- or high-resolution mass spectrometer (MS) for the determination of the airborne concentration of selected volatile organic hazardous air pollutants (oHAPs) such as ethylene oxide or vinyl chloride.

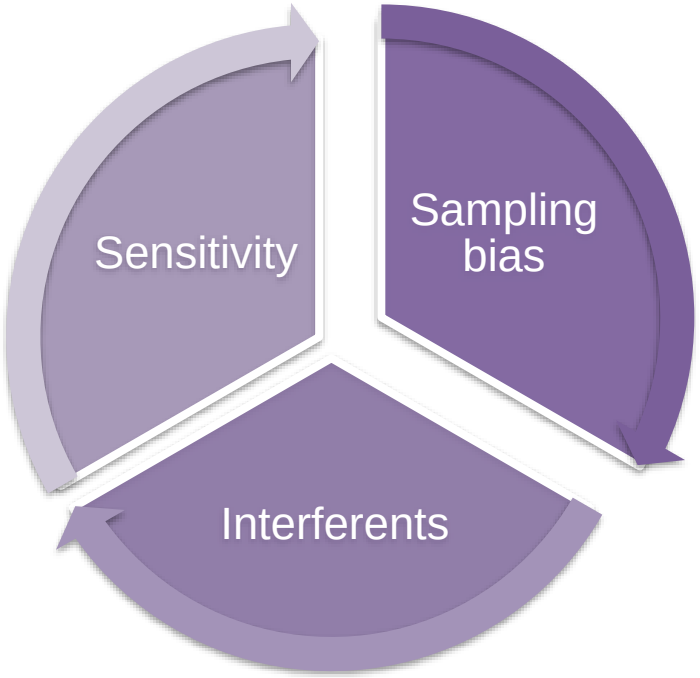
1.2 Applicability. The use of this method is strictly intended for determining airborne concentrations of selected speciated oHAPs to determine compliance with a fenceline emission standard and/or work practices when specified by the applicable regulation. This method includes data quality objectives (DQOs) specific to the measurement of airborne concentrations of speciated oHAPs and must not be used for other compliance purposes (i.e., measurements from ducted sources).

1.3 The analytical approach for this method uses a GC coupled with a low- or high-resolution MS, which may consist of a linear quadrupole, ion trap, or time-of-flight (TOF) system.

Challenges for monitoring Ethylene Oxide



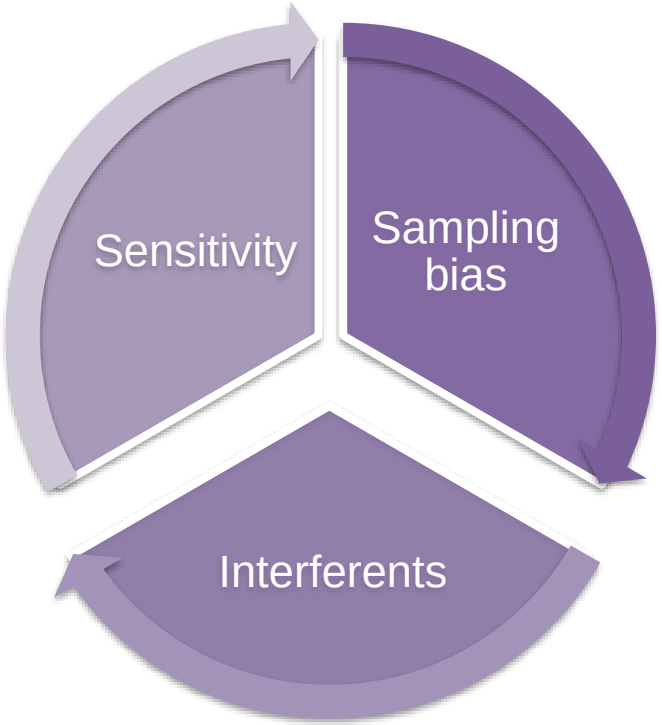
Challenges for monitoring Ethylene Oxide



- Formation/growth of EtO in canisters (humid air matrix)
- Canister inner lining appears to have an effect
  - **Silicon-ceramic lined**
  - Electropolished
  - SUMMA lined (discontinued)
- Canister to canister variation
- Effects diminished over time with repeated cleanings

TO-15A requirements a must

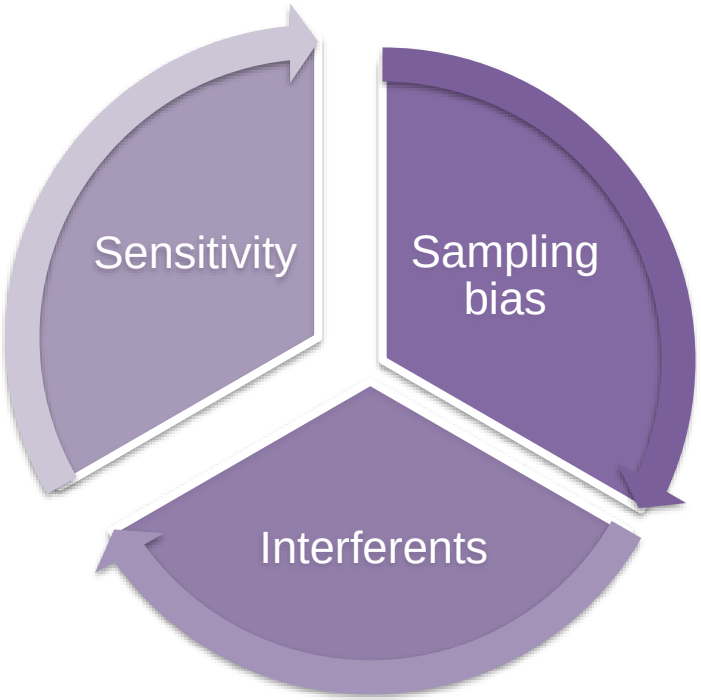
Challenges for monitoring Ethylene Oxide



- Interferents can be chromatographic or spectral
  - EtO has both
- Non-polar columns can result in analyte shifting
  - Making management of interferents more difficult
- Only 2 viable ions for quantitation
  - 44, 29,
  - 43, 42, 15 could be used for qual
  - All very common fragments

Polar/semi-polar column and assess 44 and 29 ions for quant

Challenges for monitoring Ethylene Oxide



- Small molecule
- MS sensitivity is poor
- BFB tune vs manufacturer recommended tune
  - BFB tune typically results in worse sensitivity
- Typical sample volumes taken from the canister in 100 – 1000 mL range

Check max sample volume and use the manufacturer recommended tune

Analytical instrumentation

Canisters:	6L SilcoCans with air as balance gas
Pre-concentrator:	UNITY-CIA *Advantage*-xr
Water removal:	Kori-xr
Focusing trap:	U-TO15-KXR
GC:	Agilent 8890B
Column:	DB-624MS 60m x 0.32mm x 1.8µm
MS:	5977B
Standards:	65 component 1 ppm TO-15 mix
	56 component 1 ppm PAMS mix
	Custom 1 ppm aldehyde mix
	Ethylene oxide in methanol 50mg/mL

Analytical performance

What are we aiming for?

- Focus on oHAPS NATTS list for this project
- Try to match 18ppt EtO detection limit in Restek paper
  - Non-cryo-oven approach
- Maintain TO-15A performance - previously validated

Hoisington, J.; Herrington, J.S. Rapid Determination of Ethylene Oxide and 75 VOCs in Ambient Air with Canister Sampling and Associated Growth Issues. Separations **2021**, 8, 35. https://doi.org/10.3390/separations8030035

Target compounds and their previous TO-15A performance (if tested)

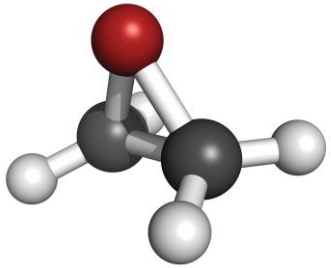
*Compound present in the method blank

Compound	Avg. RF RSD	MDL (pptv)
Propene	4.487	14.41
Chloromethane	5.787	27.37
Butadiene	20.098	5.41
Vinyl Chloride	12.339	3.21
Acetaldehyde		
Ethylene oxide		
Ethanol	25.068	*419.27
Acrolein	13.186	*70.94
Chloroform	9.129	2.32
Benzene	6.534	6.10
Trichloroethene	8.912	2.45
Tetrachloroethene	26.740	2.67
Naphthalene	11.144	8.36

Method development stages

Breakthrough volume → Optimise chromatography → Optimise MS parameters → Manage water → Maximise sensitivity

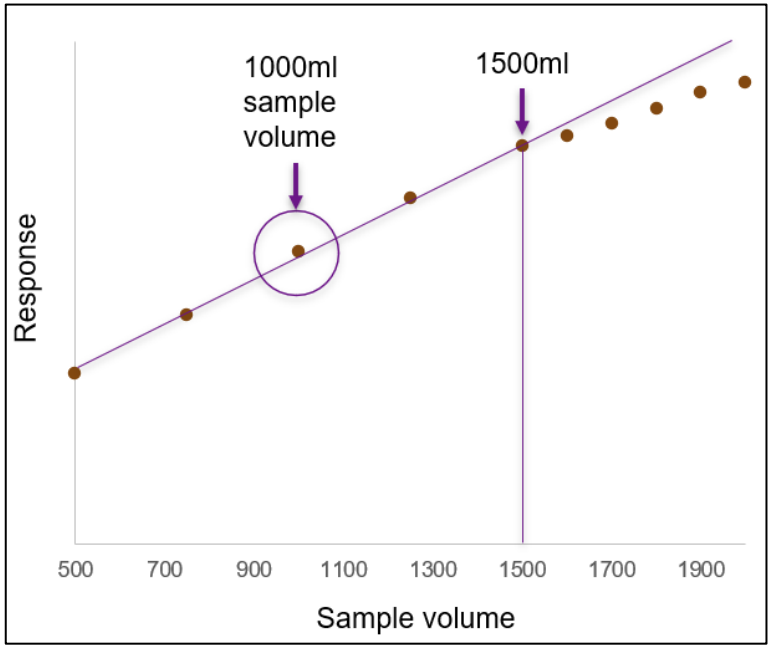
Breakthrough volume	Optimise chromatography	Optimise MS parameters	Manage water
Increase sample volume = easy way to increase sensitivity	Multiple known interferents	Stability and signal could be boosted	Water can interfere with performance of the more volatile species



How much could be sampled?

Breakthrough volume for EtO

- Typically wouldn't go beyond 1000mL for TO-15A
- Breakthrough volume = 1500 mL
  - (50mL/min sample flow)
- 1000mL picked, room to increase
- **Future work:** 20 minute sampling window so will reduce if practical or assess increased flow rates

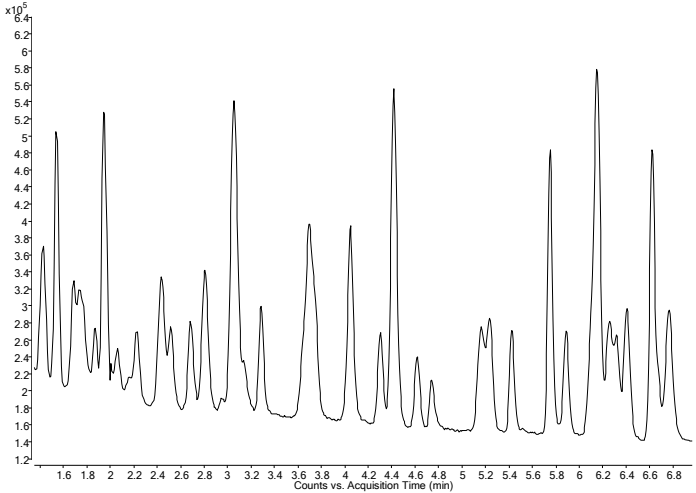


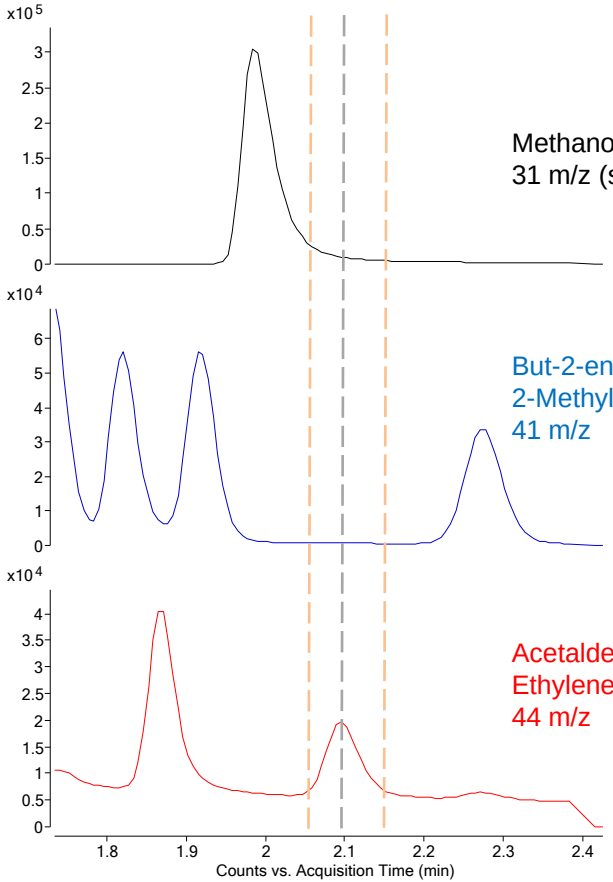
Managing interferents

Key interferents:

- Acetaldehyde
- Methanol
- Trans-2-butene
- Ethyl-nitrite
- 2,2 dimethylpropane

} Chosen to test





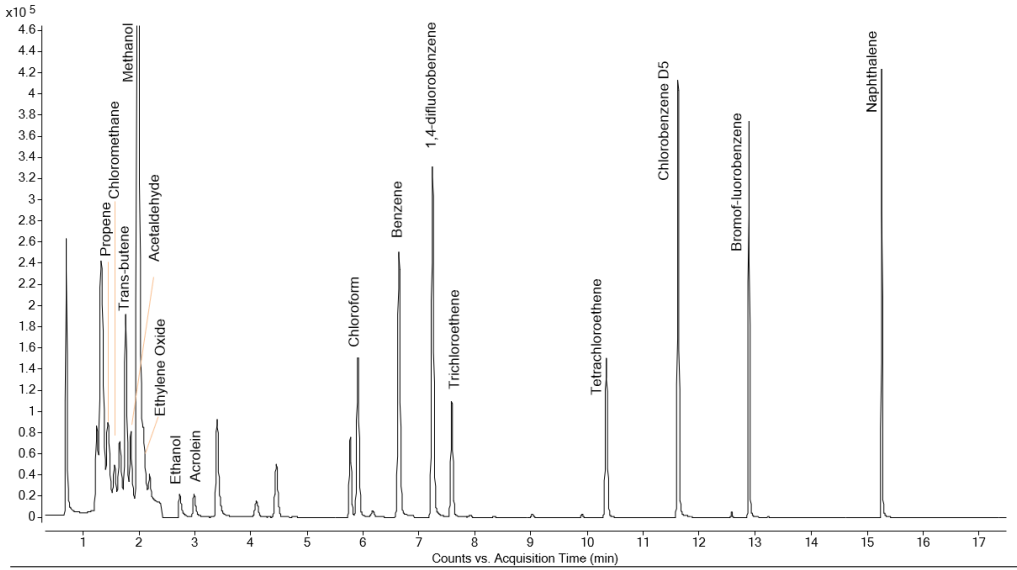
Methanol (2 mins)
31 m/z (shares 29 ion with EtO)

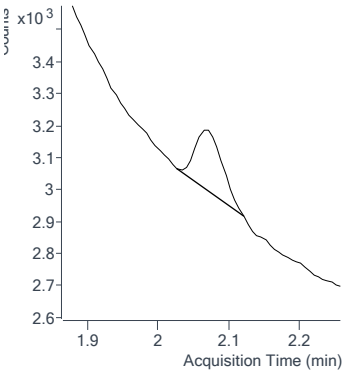
But-2-enes (1.85 & 1.95 mins)
2-Methylbutane (2.28 mins)
41 m/z

Acetaldehyde (1,88 mins)
Ethylene oxide (2.1 mins)
44 m/z

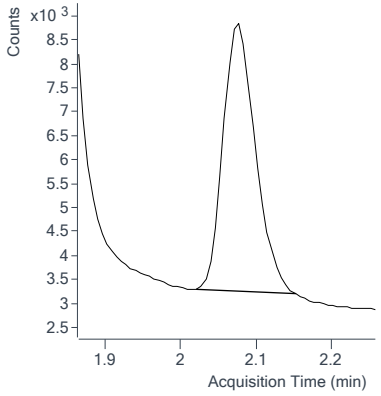
Optimising the chromatography and MS parameters

- **Chromatography:** Ongoing – looking at column phases with Agilent
- **MS parameters:** Explored increases to gain, source temperatures, parameters such as “trace ion detection” and the effect of SIM/Scan vs SIM only
- Best results with no gain, high temps, and SIM only





Ethylene oxide 20 ppt (slope is CO_2)

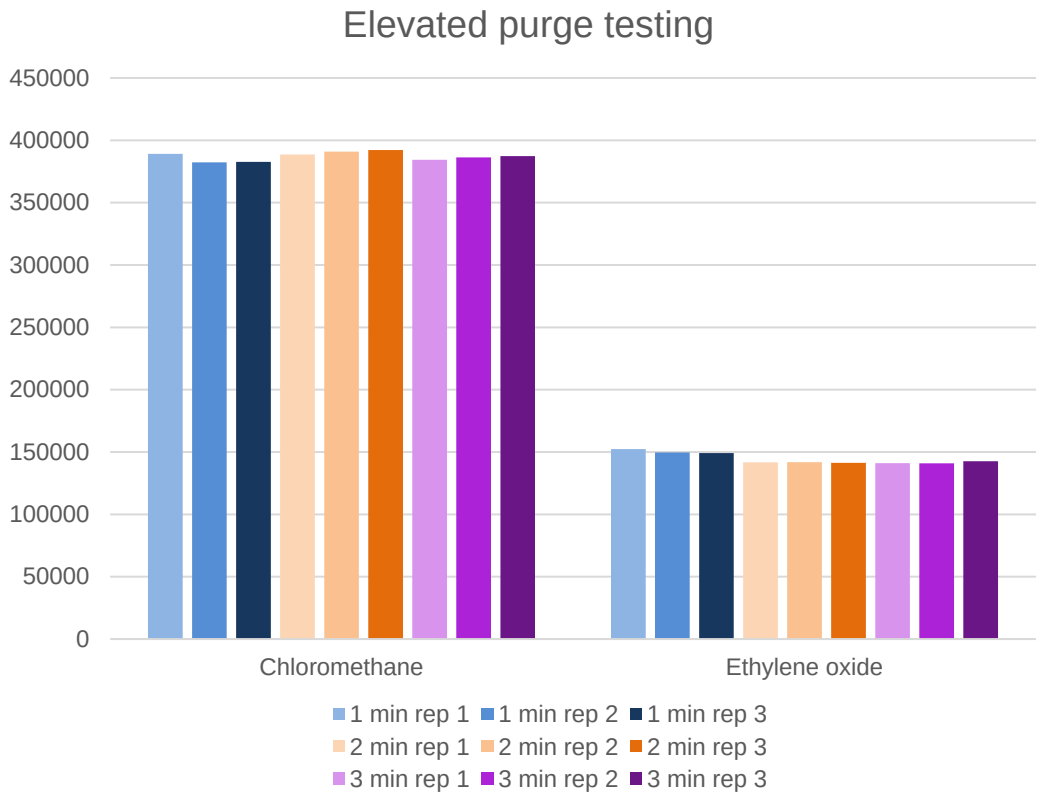


Ethylene oxide 500 ppt

Control of interferents

Managing water

- DryFocus3 mechanism used for water management – already validated for 75 species monitored in TO-15A
- 2.95% RSD for EtO over the 9 reps so no losses observed
- Chloromethane also shows good %RSD



Analytical performance

Priority NAATS compounds +

- Preliminary results

- Really impressed – plan to challenge the system and conduct more MDL studies

Compound	Linearity (RF RSD)	%RSD 1 ppb (n = 10)	MDL (ppt)
Propene	2.02%	0.98%	1.0
Chloromethane	19.54%	0.60%	5.6
Butadiene	8.16%	0.64%	4.6
Vinyl Chloride	5.14%	0.44%	3.7
Acetaldehyde	19.35%	3.63%	26
Ethylene oxide	9.49%	1.04%	14.7
Ethanol	9.04%	2.67%	68
Acrolein	2.36%	0.97%	11
Chloroform	13.00%	0.30%	5.5
Benzene	25.72%	0.35%	3.3
Trichloroethene	9.79%	0.59%	3.1
Tetrachloroethene	4.94%	0.46%	0.4
Naphthalene	13.04%	4.50%	9.3
Average	10.89%	1.32%	11.2
Min	2.02%	0.30%	0.4
Max	25.72%	4.50%	68.0

Analytical performance

Priority NAATS compounds +

- Interesting to see lab to lab differences for TO-15A (blue)
- Established lab (1) versus newly installed lab (2)
- Acetaldehyde also has good performance.

			Lab 2	Lab 1	
Compound	Linearity (RF RSD)	%RSD 1 ppb (n = 10)	MDL (ppt)	*RF RSD*	*MDL (pptv)*
Propene	2.02%	0.98%	1.0	*4.49%*	*14*
Chloromethane	19.54%	0.60%	5.6	*5.79%*	*27*
Butadiene	8.16%	0.64%	4.6	*20.10%*	*5*
Vinyl Chloride	5.14%	0.44%	3.7	*12.34%*	*3*
Acetaldehyde	19.35%	3.63%	26		
Ethylene oxide	9.49%	1.04%	14.7		
Ethanol	9.04%	2.67%	68	*25.07%*	**419*
Acrolein	2.36%	0.97%	11	*13.19%*	**71*
Chloroform	13.00%	0.30%	5.5	*9.13%*	*2*
Benzene	25.72%	0.35%	3.3	*6.53%*	*6*
Trichloroethene	9.79%	0.59%	3.1	*8.91%*	*3*
Tetrachloroethene	4.94%	0.46%	0.4	*26.74%*	*3*
Naphthalene	13.04%	4.50%	9.3	*11.14%*	*8*
Average	10.89%	1.32%	11.2	*13.03%*	*8*
Min	2.02%	0.30%	0.4	*4.49%*	*2*
Max	25.72%	4.50%	68.0	*26.74%*	**419.27*

Summary

- Preliminary results are promising and will meet the requirements of draft method 327
- Robust SOPs will be needed for managing sampling bias
- Sensitivity can be improved by increasing sample size
- Interferents can be managed but there are still challenges
- SIM only does make a difference for the detection limit
- TO-15A method was easily transferred between labs

Future work

- Continuation of work on the separation
- Testing different levels of humidity
- Conversion of the method to H_2 carrier

- Real samples - get in touch if you have any and are interested to see performance

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Markes International, UK

Contact Markes

enquiries@markes.com

UK: +44 (0)1443 230935

USA: +1 866-483-5684 (toll-free)

Germany: +49 (0)69 6681089-10

P.R. China: +86 21 5465 1216

www.markes.com
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